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(54) Pigment ink for ink jet printer

(57) An ink for an ink jet printer, characterized by comprising water, a pigment, and a polymeric material which is insoluble or sparingly soluble in water and hydrophilic, the pigment being coated with the polymeric material which is insoluble or sparingly soluble in water and hydrophilic. The ink is produced by, for example, dissolving a polymeric material which is insoluble or sparingly soluble in water and hydrophilic, such as an isobutylene/maleic anhydride copolymer resin, a nylon copolymer, polyvinyl isobutyl ether, or polyvinyl ethyl ether, in an organic solvent compatible with water, such as THF (tetrahydrofuran) or DMF (dimethylformamide), adding a pigment to the resulting solution, dispersing the mixture by means of a bead mill or the like, and evaporating the organic solvent.

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DESCRIPTION

Pigment-Containing Ink for Ink Jet Printers

TECHNICAL FIELD

The present invention relates to an aqueous ink for ink jet printers having a low viscosity and a high dispersibility and containing a pigment of high concentration.

BACKGROUND ART

As printing inks, dye-containing inks in which a dye is dissolved in a solvent as a colorant, and pigment-containing inks in which a solid pigment is dispersed in a liquid medium as a colorant are available. The pigment-containing ink generally exhibits no discoloration, maintains a fast color, and is excellent in sharpness, compared with the dye-containing ink.

Conventional inks for ink jet printers are primarily dye-containing inks. These inks, however, have disadvantages with regard to bleeding, light resistance, water resistance, etc. Accordingly, the use of pigment-containing inks is desired. To overcome such disadvantages, inks containing a pigment such as carbon black, aniline black, etc. have been conceived as disclosed in Japanese Unexamined Patent Publication (kokai) Nos. 61-283875, 64-6074 and 1-31881. The pigment-containing inks disclosed in these patent publications, however, have the disadvantages that these inks fix poorly on recording media such as paper sheets, and that agglomeration and sedimentation take place in the ink liquid when the inks contain pigments at high concentration. As a result, the concentration of the pigments in the inks for ink jet printers is required to be low. Japanese Unexamined Patent Publication (Kokai) No. 5-331395 discloses an ink for ink jet printers in which particles are stabilized. The ink disclosed therein contains water, a colorant and a water-soluble polymer

such as a polyvinyl alcohol.

DISCLOSURE OF INVENTION

To prevent a nozzle from clogging, a pigment-containing ink having a still lower viscosity and a high dispersibility is desired. An object of the present invention is to provide an ink having a relatively low viscosity and a high dispersibility, and containing a pigment at high concentration. Since a water-insoluble or sparingly water-soluble polymer material is used in the ink at the present invention, the polymer material is not distributed over the entire dispersion system, but is coated onto the surface of the pigment particle's. As a result, it is possible to provide an ink having a low viscosity and a high dispersibility, and containing a pigment at high concentration.

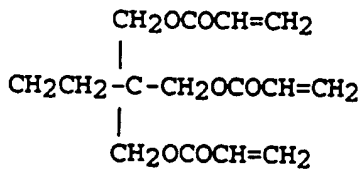
The ink for ink jet printers of the present invention comprises water, a pigment and a water-insoluble or sparingly water-soluble, hydrophilic polymer material, and is characterized in that the pigment is coated with the polymer material.

BEST MODE FOR CARRYING OUT THE INVENTION

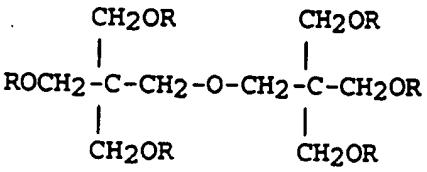
The ink is produced, for example, by dissolving a water-insoluble or sparingly water-soluble, hydrophilic polymer material such as isobutylene-maleic anhydride copolymer resins, copolymerized nylons, poly(vinyl isobutyl ether) and poly(vinyl ethyl ether) in an organic solvent miscible with water such as THF (tetrahydrofuran) and DMF (dimethylformamide), adding a pigment, dispersing the pigment with a bead mill, etc., and evaporating the organic solvent. The dispersibility of the pigment can thus be improved by coating the pigment with the water-insoluble or sparingly water-soluble hydrophilic polymer material, and as a result, the sedimentation of the pigment can be prevented. Moreover, since the tackiness of such a polymer material itself is high, the adhesion of the pigment to a printing medium such as a printing sheet can be improved.

The ink of the present invention may further contain UV-ray-curable monomer(s) or oligomer(s). When a medium (paper sheet) is printed with the ink of the present invention containing a curable monomer or oligomer, the ink can be fixed thereon by irradiating the medium with a UV-light lamp (e.g., 10 mW/cm^2) so that the monomer or oligomer is instantaneously cured. Since such an ink contains a monomer or oligomer having a low viscosity, the ink has the advantage that clogging on the head does not take place because the ink as a whole has a low viscosity and does not cure until UV-rays are irradiated. The UV-ray-curable monomer or oligomer may be any conventional UV-ray-curable monomer or oligomer. Examples thereof include TMPTA, DPHA, D-310, D-330 and MANDA (trade name, manufactured by Nippon Kayaku Co., Ltd.). These have the following respective chemical formulas:

TMPTA

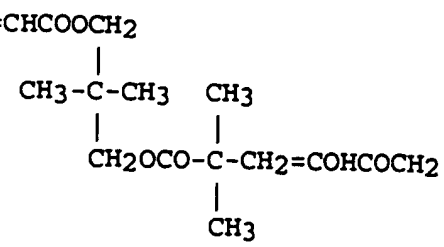


DPHA, D-310, D-330



wherein five of the R groups are acryloyl and one of the R groups is alkynoyl, or three of the R groups are acryloyl and three of the R groups are alkynoyl, or a mixture of a compound in which all R groups are acryloyl and a compound in which five of the R groups are acryloyl and one R group is hydroxyl, and

MANDA



Conventional polymerization initiators such as 2,4-diethylthioxanthone and benzophenone may be used as polymerization initiators for UV-ray curing.

Useful pigments of the present invention include all inorganic and organic pigments used in conventional pigment-containing inks, for example, synthetic inorganic pigments such as carbon black, alumina, barium sulfate, chrome yellow and titanium white and synthetic organic pigments such as azo pigments, lake pigments from basic dyes and phthalocyanine pigments. Furthermore, various metals and their oxides, etc. may also be used as pigments.

The useful particle size of the pigments is from 0.01 to 1 μm (micron), particularly preferably from 0.01 to 0.5 μm (micron).

When an organic pigment is used, the ink of the present invention may contain up to about 10% by weight of the organic pigment based on the whole ink composition and, generally, from 1 to 5% by weight being preferred. When an inorganic pigment is used, the ink may contain up to about 20% by weight of the inorganic pigment, generally from 3 to 10% by weight.

EXAMPLES

The present invention will be illustrated in more detail by making reference to examples, but the present invention is in no way limited thereto.

Example 1

In a bead mill equipped with a temperature control unit, 100 g of THF (tetrahydrofuran), 8 g of a pigment

(trade name, Mitsubishi Carbon #230) and 12 g of a isobutylene-maleic anhydride copolymer resin were placed, and dispersed at 40°C for about 15 minutes until the resulting particle size became no more than 0.5 μm (micron). The dispersion in an amount of 120 g thus obtained was placed in a solvent-separating apparatus (distillation column), and 1,000 g of distilled water was further added, followed by heating and stirring the mixture to emulsify it. THF was then evaporated until the THF content became no more than 0.01% based on the weight of water, and then water was evaporated until the water content in the mixture became 80 g. The ink thus obtained is referred to as Dispersion Ink A.

50 parts by weight of Dispersion Ink A, 40 parts by weight of distilled water, 5 parts by weight of diethylene glycol and 5 parts by weight of ethyl alcohol were stirred and mixed by a supermill dispersion mixer (manufactured by Inoue Seisakusho K.K.), followed by filtering the mixture through a filter (0.5 μm (micron)) to obtain an ink. The ink had a viscosity of 2.8 cP at 20°C, and contained 4% by weight of the pigment.

Example 2

To investigate the effects of a curable monomer contained in the ink, 50 parts by weight of Dispersion Ink A, 48 parts by weight of TMPTA and 2 parts by weight of benzophenone were stirred and mixed by a supermill dispersion mixer (manufactured by Inoue Seisakusho K.K.), followed by filtering the mixture through a filter (0.5 μm (micron)) to obtain an ink. The ink had a viscosity of 2.1 cP at 20°C, and contained 4% by weight of the pigment.

Comparative Example 1

In a bead mill connected to a temperature control unit, 92 g of water and 8 g of the same pigment as employed in Example 1 were dispersed at 40°C for about 15 minutes until the resulting particle size was no more than 0.5 μm (micron). The ink thus obtained is referred to as Dispersion Ink B.

50 parts by weight of Dispersion Ink B, 40 parts by weight of distilled water, 5 parts by weight of diethylene glycol and 5 parts by weight of ethyl alcohol were stirred and mixed by a supermill dispersion mixer (manufactured by Inoue Seisakusho K.K.), followed by filtering the mixture through a filter (0.5 μm (micron)) to obtain an ink. The ink had a viscosity of 1.8 cP at 20°C, and contained 4% by weight of the pigment.

Testing Method

* Test in the Environment for Use (Test 1)

Samples produced in Example 1 and Comparative Example 1 as described above were kept in respective sample bottles at 5°C and 40°C for 3 months.

* Preservation Test in the Environment for Packing (Test 2)

The samples were kept in respective sample bottles at -5 to 70°C for 3 months.

Tests 3 to 6 described below were conducted using a jet printer (trade name of FMJP 201 manufactured by Fujitsu Ltd.) of the thermal ink jet type. The ink produced in Example 2 was cured for 1 second using a UV-light lamp at an intensity of 10 mW/cm^2.

* Discharge Stability (Test 3)

Continuous discharge of 1,000 sheets was conducted at room temperature (25°C), 5°C and 40°C, and the recording stability was measured.

* Printing Density (Test 4)

Commercially available recycled paper sheets (WR paper sheets manufactured by Xerox) were printed to give specimens, and the density thereon was measured by a Macbeth densitometer.

* Printing Quality (Test 5)

The recycled paper sheets mentioned above were printed with one dot, and the expantion of the dot diameter (bleeding) of each dot and the circularity of the dot were judged with an optical microscope.

* Adhesion Fixation of Printed Characters (Test 6)

A paper sheet immediately after being printed was rubbed with the same type of paper sheet, and the resultant stain was visually judged.

Test No.	Example 1	Example 2	Comp. Example 1
1	◎	o	x
2	o	o	x
3	◎	◎	x
4	1.2	1.2	0.9
5	◎	◎	x
6	o	◎	x

Note: The results were judged on the following criteria.

Tests 1 and 2

Neither separation of the recording liquid nor sedimentation therein is observed.---------- ◎

Although the separation of the recording liquid takes place to a slight extent, no sedimentation is observed and the recording liquid is restored to its original state with light shaking.---------- o

The separation of the recording liquid is observed, and the recording liquid is not restored to its original state with light shaking.---------- x

Test 3

Stabile discharge ---------- o

Discharge with irregularities ---------- x

Test 5

A printed dot with little bleeding and high circularity ---------- ◎

A printed dot with much bleeding and low circularity ---------- x

Test 6

No stain is observed. ---------- ◎

Although printed characters are good, the printed sheet is slightly stained on rubbing when the sheet has been entirely printed.

---------- o

The peripheries of printed characters are stained on rubbing. ---------- x

Although a thermal ink jet printer manufactured by Fujitsu Ltd. was used in these examples, similar results will be obtained with another thermal printer or piezo ink jet printer.

INDUSTRIAL APPLICABILITY

The use of a water-insoluble or sparingly water-soluble, hydrophilic polymer material such as isobutylene-maleic anhydride copolymer resin increases the stability of an aqueous dispersion of a pigment coated therewith, and improves the adhesion of the pigment to the medium (paper sheet) during printing due to the tackiness of the polymer material.

The addition of a UV-ray-curing monomer or oligomer lowers the viscosity of the ink as a whole, and no curing takes place so long as UV-rays are not irradiated. Accordingly, no clogging takes place on the head.

Printing can thus be conducted with a pigment-containing ink excellent in resistance to water and light in place of a dye-containing ink.

CLAIMS

1. An ink for ink jet printers which comprises water, a pigment and a water-insoluble or sparingly water-soluble, hydrophilic polymer material, and which is characterized in that said pigment is coated with said water-insoluble or sparingly water-soluble, hydrophilic polymer material.

2. The ink for ink jet printers as claimed in claim 1, wherein said ink further comprises a dispersion of a UV-ray-curing monomer or oligomer.

3. The ink for ink jet printers as claimed in claim 1 or 2, wherein said polymer material is a material selected from the group consisting of isobutylene-maleic anhydride copolymer resins, copolymerized nylons, poly(vinyl isobutyl ether) and poly(vinyl ethyl ether).

4. The ink for ink jet printers as claimed in claim 1 or 2, wherein said pigment is a synthetic inorganic pigment selected from the group consisting of carbon black, alumina, barium sulfate, chrome yellow and titanium white.

5. The ink for ink jet printers as claimed in claim 1 or 2, wherein said pigment is a synthetic organic pigment selected from the group consisting of azo pigments, lake pigments from basic dyes and phthalocyanine pigments.

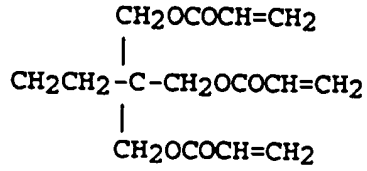
6. The ink for ink jet printers as claimed in claim 1 or 2, wherein said pigment is a metal or an oxide thereof.

7. The ink for ink jet printers as claimed in claim 4, wherein said ink comprises up to 20% by weight of said pigment based on said ink.

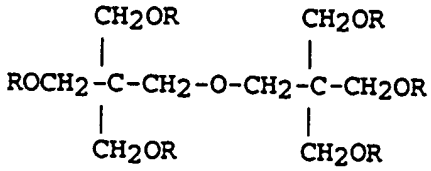
8. The ink for ink jet printers as claimed in claim 5, wherein said ink comprises up to 10% by weight of said pigment based on said ink.

9. The ink for ink jet printers as claimed in claim 1 or 2, wherein the particle size of said pigment is from 0.01 to 1 μm (micron).

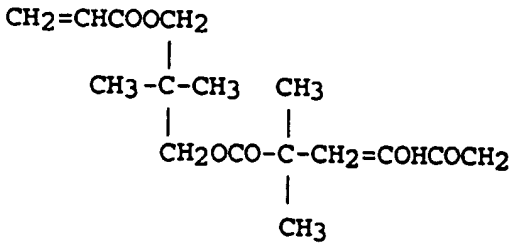
10. The ink for ink jet printers as claimed in claim 2, wherein said UV-ray-curing monomer is a monomer selected from the group consisting of



or



wherein five of the R groups are acryloyl and one R group is alkynoyl, or three of the R groups are acryloyl and three of the R groups are alkynoyl, or a mixture of a compound in which all of the R groups are acryloyl and a compound in which five of the R groups are acryloyl and one R group is hydroxyl, and



or said UV-ray-curing oligomer is an oligomer resulting from said monomers.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/00696

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl[6] C09D11/00, C09C3/10
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
Int. Cl[6] C09D11/00-11/20, C09C3/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 4-227668, A (E.I. Du Pont de Nemours and Co.), August 17, 1992 (17. 08. 92) & US5085698	1 - 10
A	JP, 2-103274, A (Dainichiseika Color & Chemicals Mfg. Co., Ltd.), April 16, 1990 (16. 04. 90) (Family: none)	1 - 10
A	JP, 5-247370, A (Dainichiseika Color & Chemicals Mfg. Co., Ltd.), September 24, 1993 (24. 09. 93) & EP635380	1 - 10
A	JP, 6-25572, A (Seiko Epson Corp.), February 1, 1994 (01. 02. 94) (Family: none)	1 - 10
A	JP, 2-311570, A (Brother Industires, Ltd.), December 27, 1990 (27. 12. 90) (Family: none)	1 - 10
A	JP, 3-216379, A (Canon Inc.), September 24, 1991 (24. 09. 91) (Family: none)	1 - 10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
April 12, 1996 (12. 04. 96)	April 23, 1996 (23. 04. 96)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)